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AUTHOR(S):

Masai, Hirokazu; Yanagida, Takayuki; Fujimoto, Yutaka; Koshimizu, Masanori; Yoko, Toshinobu

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## Scintillation property of rare earth-free SnO-doped oxide glass

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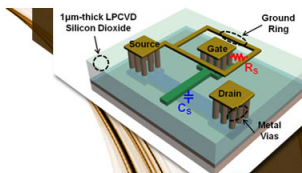
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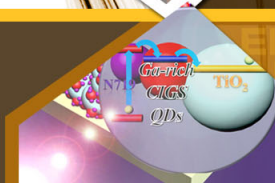
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## Scintillation property of rare earth-free SnO-doped oxide glass

Hirokazu Masai,<sup>1,a)</sup> Takayuki Yanagida,<sup>2</sup> Yutaka Fujimoto,<sup>3</sup> Masanori Koshimizu,<sup>4</sup> and Toshinobu Yoko<sup>1</sup>

<sup>1</sup>Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

<sup>2</sup>Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196, Japan

<sup>3</sup>Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

<sup>4</sup>Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Sendai 980-8579, Japan

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The authors have demonstrated scintillation of rare earth (RE)-free Sn-doped oxide glass by excitation of ionizing radiation. It is notable that light emission is attained for RE-free transparent glass due to  $s^2$ - $sp$  transition of  $\text{Sn}^{2+}$  centre and the emission correlates with the excitation band at 20 eV. We have also demonstrated that excitation band of emission centre can be tuned by the chemical composition of the host glass. The present result is valuable not only for design of RE-free inorganic amorphous oxide scintillator but also for revealing the band structure of oxide glass by irradiation of ionizing radiation. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4766340>]

Scintillation consisting of prompt luminescence and photostimulated luminescence has been widely used in a variety of fields, for example, medical (x-ray CT, PET, flat panel detector), security (luggage inspection system), environmental monitoring, basic science, and so on. Nowadays, requirement of scintillators for environmental monitoring has been increasing, especially in Japan after the Tohoku earthquake. On the other hand, scintillators possessing higher quantum efficiency have been investigated throughout the world especially from a security point of view. Since such scintillators are usually used in bulk shape whose size is several meters, design of both chemical composition and fabrication process is important for preparation of large practical scintillators.

Because of the high detection ability, conventional crystalline scintillators contain rare earth (RE) in host matrices, for example,  $\text{Gd}_3(\text{Ga}, \text{Al})_5\text{O}_{12}$  (Ref. 1) and  $\text{Lu}_2\text{SiO}_5$  (Ref. 2) that are used in a survey meter and medical applications, respectively. On the other hand, there are some scintillators composed of ubiquitous elements, such as  $\text{SrI}_2$  or  $\text{NaI}$ .<sup>3,4</sup> However, despite the high quantum efficiency,<sup>3–5</sup> the practical application of such scintillators is limited because of the severe deliquescent. Sulfides, another ubiquitous scintillator possessing the narrow band gap, have neither been a candidate, because it is actually difficult to fabricate transparent bulk material. Practical use of scintillators composed of ubiquitous elements, therefore, has been greatly limited.

Although there are self-activated materials, such as BGO or  $\text{CdWO}_4$ , the RE-containing materials have attracted much attention from viewpoint of materials design. In this way, most of recent scintillators contain RE in the host matrix, which is a quite opposite trend of recent rare metal-free material. In addition, the performance improvement of such scintillators has been achieved by substitution of small amounts of RE elements, which is fully depending on the rule of thumb. For example, only conventional design using REs, such as Gd and

Lu, has been used for the applications,<sup>6,7</sup> although recent knowledge of phosphor material concerning photoluminescent material could be available. It is expected that such divergence in material design between radioluminescence and photoluminescence is due to the difference of emission mechanism. Scintillation mechanism is typically described by energy transition from an irradiated host matrix to an emission centre via energy transfer. However, the energy transfer process is not fully clarified, that is why a large part of mechanism is still academically untapped. Since there are both self-activated scintillators and emission centre-containing scintillators with the optimum concentration, it should be said that the essential origin of scintillation may be wide-ranging. Therefore, the authors have expected that randomness is not a critical factor for the effective emission and emphasized that scintillation can be attained even in RE-free amorphous oxide glass. Although Li-glass (Saint-Gobain K.K.) has been actually used as a scintillator from the 1960s,<sup>8,9</sup> it is very difficult to prepare the homogeneous bulk sample suitable for the practical application. If glass material without the RE cation shows scintillation behaviour comparable to the crystalline phosphor, it will be considered a scintillator capable of good formability and productivity that are important in the industrial manufacturing process. Such emitting material is quite different from the conventional RE-doped crystalline scintillator.

In the study, we have focused on the  $ns^2$ -type emission centre<sup>10</sup> as an activator in oxide glass. Since the  $ns^2$ -type emission centres ( $n \geq 4$ ) possess an allowed transition of  $s^2$ - $s^1p^1$ , these ubiquitous species can be an alternative to RE emission centre. As mentioned above, conversion efficiency of scintillation, in which energy transfer from host to activator occurs, is strongly affected by the amount of emission centre. Considering characteristics of the  $ns^2$ -type emission centres, we have speculated that the emission centre is suitable for amorphous glass, because maximum amount of  $ns^2$ -type emission centre in glass is usually larger than that of crystal. Recently, Masai *et al.* reported high QE value for amorphous  $\text{SnO-ZnO-P}_2\text{O}_5$  low-melting glass.<sup>11,12</sup> It is notable that the transparent glass containing no RE cation

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: masai\_h@noncry.kuicr.kyoto-u.ac.jp. Tel.: +81-774-38-3131. Fax: +81-774-33-5212.

shows efficient UV-excited emission that is comparable to crystal phosphor such as  $\text{MgWO}_4$ ; further, this was the largest efficiency of glass material without RE cation ever reported. The emission was brought about by  $\text{Sn}^{2+}$ , which is the most common and harmless  $ns^2$  type centre.<sup>9</sup> The previous results suggest that  $\text{Sn}^{2+}$  can be an effective emission centre of the scintillation material because of the allowed transition. In the present study, we have demonstrated that scintillation is attained using RE-free amorphous oxide glass containing  $\text{Sn}^{2+}$  emission centre.

The present  $\text{SnO-SrO-B}_2\text{O}_3$  and  $\text{SnO-ZnO-P}_2\text{O}_5$  glasses were prepared according to a conventional melt-quenching method that employs a platinum crucible. In the borate system, the starting chemicals ( $\text{SnO}$ ,  $\text{SrCO}_3$ , and  $\text{B}_2\text{O}_3$ ) were melted at  $1100^\circ\text{C}$  for 30 min in the ambient atmosphere. In the case of phosphate system, the experimental details are shown in another paper.<sup>13</sup> The glass melt was quenched on a steel plate at  $200^\circ\text{C}$  and then annealed for 1 h at the glass transition temperature,  $T_g$ , as measured by differential thermal analysis operated at a heating rate of  $10^\circ\text{C}/\text{min}$  using TG8120 (Rigaku). Size of the samples for the measurements was  $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$ .

Radioluminescence measurements were done by using the spectrofluorometer FLS920 (Edinburgh Instruments) as a detector. The excitation sources of FLS920 were put off and only the detector part was utilized. The radioisotope which was used in the radioluminescence measurements was  $4\text{ MBq }^{241}\text{Am}$ , because its 5.5 MeV alpha-ray could be fully absorbed easily and its energy deposits are enough to detect scintillation photons in such a photon-integrated type experiment. Unfortunately, we did not have an adequate optical filter, and the observation was done up to 600 nm. In order to avoid to detect emission lines from the air due to the ionization by  $\alpha$ -rays, the radioisotope was directly attached to the sample scintillators to cover whole the  $\alpha$ -ray emitting region. The schematic setup is shown in the previous paper.<sup>14</sup>

Scintillators were coupled with photomultiplier tube (PMT) R7600 fabricated by Hamamatsu. The optical grease was used to optically contact the PMT, and several layers of Teflon tapes were used to wrap the scintillator to collect scintillation photons with high efficiency. Upon  $\alpha$ -ray or neutron irradiation in the scintillator, the signal from the anode of PMT was fed into preamplifier (ORTEC 113), shaping amplifier (ORTEC 572) with  $10\text{ }\mu\text{s}$  shaping time, and multi-channel analyser (Amptek Pocket MCA), in order. The excitation radioisotope was  $^{241}\text{Am}$   $\alpha$ -ray or  $^{252}\text{Cf}$  neutron source. At the same time, the scintillation decay time was recorded using an oscilloscope (TDS3034B). The oscilloscope was terminated with a  $50\text{ }\Omega$  resistance and Lemo cable having a capacitance of around  $20\text{ pF}$  was used. The time resolution due to the experimental setup for the decay time constant was evaluated at around 1 ns. One hundred times averaging was carried out to obtain decay time profiles.

The emission and excitation spectra of samples were measured at room temperature under the irradiation of synchrotron radiation having energies of 6–20 eV at the UVSOR facility (BL-7B). In excitation spectra, the step of the wavelength was 2 nm and that of the emission spectra was 0.4 nm.

The obtained samples were transparent and colourless in the visible region. Figure 1 shows the emission spectra of

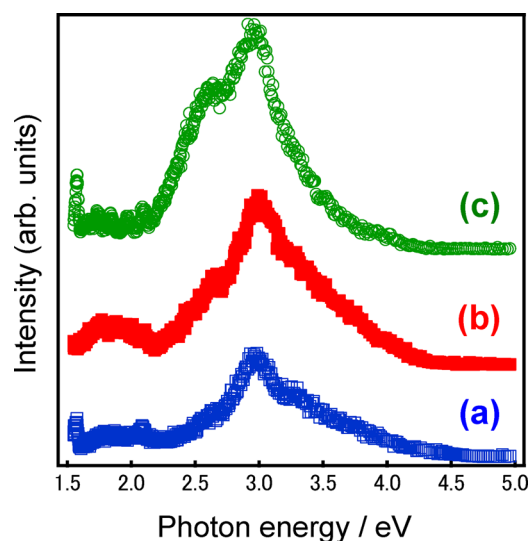


FIG. 1. Emission spectra of  $0.1\text{SnO-}24.9\text{SrO-}75\text{B}_2\text{O}_3$  (a),  $0.5\text{SnO-}24.5\text{SrO-}75\text{B}_2\text{O}_3$  (b), and  $5\text{SnO-}60\text{ZnO-}40\text{P}_2\text{O}_5$  (c) glasses by irradiation of  $\alpha$ -ray using  $4\text{ MBq }^{241}\text{Am}$  as an excitation source.

$0.1\text{SnO-}24.9\text{SrO-}75\text{B}_2\text{O}_3$  (a),  $0.5\text{SnO-}24.5\text{SrO-}75\text{B}_2\text{O}_3$  (b), and  $5\text{SnO-}60\text{ZnO-}40\text{P}_2\text{O}_5$  (c) glasses by irradiation of  $\alpha$ -ray using  $4\text{ MBq }^{241}\text{Am}$  as an excitation source. This irradiation is performed to evaluate the  $^6\text{Li}(n,\alpha)^3\text{H}$  reaction.<sup>15</sup> Broad emission, whose peak energy is 3 eV and the FWHM is about 1 eV, is clearly observed in all glasses. The broad emission is due to  $\text{Sn}^{2+}$  emission centre whose reported lifetime is typically microseconds.<sup>9</sup> These spectra show that the emission consists of at least two emission bands although the origin is not clarified yet, and that the emission bands are affected by the amount of SnO. Considering the emission intensities of samples (a) and (b), we have found that emission intensity increases with increasing amount of SnO. It is notable that the present result of radioluminescence is in clear contrast to that of photoluminescence. In the case of photoluminescence by irradiation of deep UV light, emission intensity of  $0.1\text{SnO-}24.9\text{SrO-}75\text{B}_2\text{O}_3$  glass is larger than that of  $0.5\text{SnO-}24.5\text{SrO-}75\text{B}_2\text{O}_3$  glass, because of concentration quenching of  $\text{Sn}^{2+}$  (see supplemental figure 1 (Ref. 17)). Therefore, we have concluded that the radioluminescence shows the behaviour different from the conventional UV-irradiated photoluminescence. Since the emission property of oxide glass is affected by the preparation scheme, further study is needed for examination of amorphous based scintillator not only from the viewpoint of chemical composition but also from that of preparation condition.

For evaluation of emission property, particle counting measurement, in which particles possessing the different energy were separately detected, was done. Figure 2 shows the pulse height distribution spectra of the  $0.1\text{SnO-}24.9\text{SrO-}75\text{B}_2\text{O}_3$ ,  $0.5\text{SnO-}24.5\text{SrO-}75\text{B}_2\text{O}_3$ , and  $5\text{SnO-}60\text{ZnO-}40\text{P}_2\text{O}_5$  glasses by  $^{241}\text{Am}$   $\alpha$ -ray irradiation together with that of Li-glass as a standard reference. Bottom and left axes show multichannel analyser (MCA) channel and the particle counts, respectively. The MCA channel,  $\varepsilon_{\text{MCA}}$ , which corresponds to photon energy of ionizing radiation, is calculated from the following equation:

$$\varepsilon_{\text{MCA}} = N_e \times \eta_{\text{PHM}} \times \alpha_{\text{amp}}, \quad (1)$$



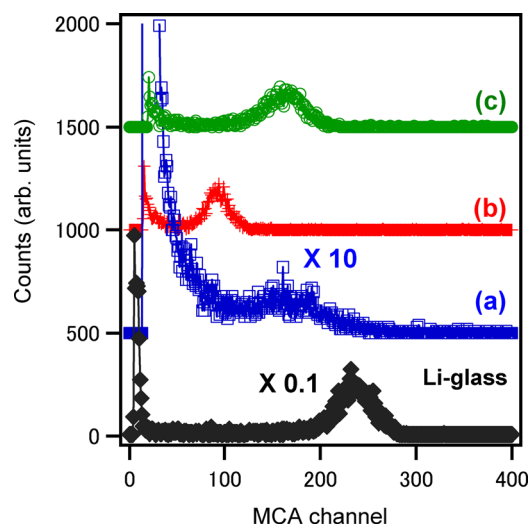


FIG. 2. Pulse height distribution spectra of the  $0.1\text{SnO}-24.9\text{SrO}-75\text{B}_2\text{O}_3$  (a),  $0.5\text{SnO}-24.5\text{SrO}-75\text{B}_2\text{O}_3$  (b), and  $5\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$  (c) glasses by  $^{241}\text{Am}$   $\alpha$ -ray irradiation together with that of Li-glass as a standard reference.

where  $N_e$ ,  $\eta_{\text{PHM}}$ ,  $\alpha_{\text{amp}}$  are amount of emission, quantum efficiency of photomultiplier, and amplification efficiency of readout electronics, respectively. Since the present spectra were measured using the identical excitation source, the counts of each MCA channel substantially show the number of photoelectron. Reference sample is the Li-glass whose amount of light emission is 6000 photon/neutron. Although the particle counts of the present glasses are lower than that of Li-glass, the present glasses show clear full energy peak by  $\alpha$ -ray irradiation, which is not a common phenomenon in amorphous materials.

Figure 3 shows emission spectra of the  $0.5\text{SnO}-24.5\text{SrO}-75\text{B}_2\text{O}_3$  glass (a) and the  $5.0\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$  glass (b) together with the contour plots. These emission spectra were measured at room temperature by excitation of the photon energy of 20.7 eV. Each contour plot shows the photon energy of excitation (ordinate) and emission (abscissa), and the intensity axes are shown on an identical linear scale. The contour plots of two glasses indicate that  $\text{Sn}^{2+}$  possesses two excitation bands: one is the  $S_0-S_2$  transition of  $\text{Sn}^{2+}$  that locates at the band edge<sup>16</sup> ( $\sim 6$  eV), and another is a band that

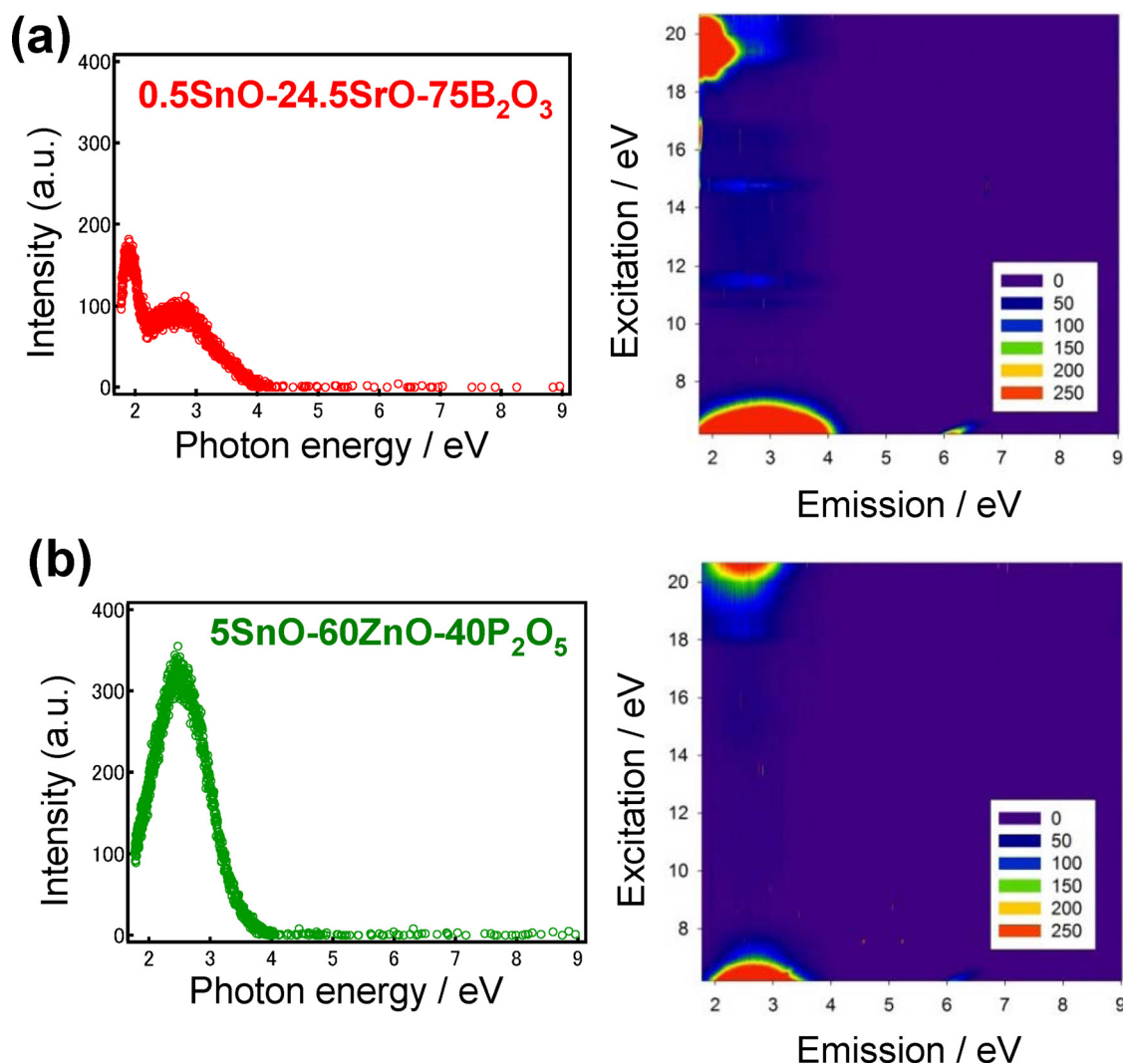


FIG. 3. Emission spectra and contour plots of  $0.5\text{SnO}-24.5\text{SrO}-75\text{B}_2\text{O}_3$  (a) and  $5\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$  (b) glasses. The emission spectra were measured at room temperature by excitation of the photon energy of 20.7 eV.

we observed at above 20 eV in the present study. Assuming that this band corresponds to the excitation in the host glass, the emission occurs via the energy transfer from the host to the  $\text{Sn}^{2+}$  emission centre. The existence of higher excitation band ensures the possibility of scintillation by ionizing radiation. One may notice that emission spectra excited by  $^{241}\text{Am}$   $\alpha$ -ray (Fig. 1) is different from the spectra shown in Fig. 3. Although the origin is not fully clarified yet, it is expected that difference in emission spectra shape originates in difference of the excitation density of excitation source. Since we have demonstrated that the higher band depends on the chemical composition of the glass (see supplemental figure 2), there is a possibility that several sites may be activated by irradiation of  $^{241}\text{Am}$   $\alpha$ -ray (5.5 MeV). The decay constants of the  $0.5\text{SnO}-24.5\text{SrO}-75\text{B}_2\text{O}_3$  and the  $5.0\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$  glasses are estimated as 0.6  $\mu\text{s}$ , 1.2  $\mu\text{s}$ , respectively. Considering the emission energy of  $\text{Sn}^{2+}$ , we conclude that the emission is due to  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  relaxation of  $\text{Sn}^{2+}$ , whose decay scale is at microseconds. The observed difference in decays and the emission peak energies are originated from difference in the coordination field of  $\text{Sn}^{2+}$  centre that is affected by the chemical composition of the mother glass. Although the emission decay of  $\text{Sn}^{2+}$  in microseconds is not fast, it is sufficient response speed for most practical application. Therefore, it is expected that the present RE-free glasses possess high potential for amorphous scintillator.

Here, we have pointed the significance of preparation of RE-free amorphous scintillator. First, RE-free scintillator is meaningful in terms of natural resource. Second, advantage of amorphous material is that various kinds of elements can be added to the glass to control the emission properties as well as to improve mechanical or thermal property, which is also applied for the conventional Li-glass. However, there are two differences between the two amorphous scintillators: (1) a greater number of emission centres,  $\text{Sn}^{2+}$ , can be doped in the present glass and (2) borate or phosphate glass can be prepared at about 300 °C lower than Li-glass which is surely

great advantage for preparation of various shape of devices. In the present study, we emphasize that the present RE-free amorphous glass containing  $\text{ns}^{2+}$ -type emission centre is an alternative candidate for crystalline scintillators from viewpoint of the formativeness. Recent social conditions surely require a scintillator, i.e., a unique and effective energy shifter, in the near future. Although we have not yet clarified the mechanism, the present RE-free inorganic amorphous materials possessing effective scintillation will be required for a great variety of science and practical applications.

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- <sup>17</sup>See supplementary materials at <http://dx.doi.org/10.1063/1.4766340> for PL-PLE contour plot of  $\text{SnO}-\text{SrO}-\text{B}_2\text{O}_3$  glass, and for that of  $\text{SnO}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  glass.